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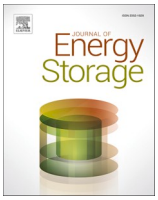

Underground gas storage as a promising natural methane bioreactor and reservoir?

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ABSTRACT

Employing deep reservoirs as UGS (underground gas storage) has a long history across continents. In 2018, 689 underground gas reservoirs with a total volume of 417 bcm were in operation worldwide. It is known that many microbial processes take place in the deep underground, even under the conditions of underground gas reservoirs. In this review, we focus mainly on methanogenesis and discuss related topics such as optimal environmental conditions, description of different types of UGS and microbial communities inhabiting these environments. We elucidate the potential of UGS as natural bioreactors for non-fossil methane production in the context of Power to Methane technology and the extension/expansion of the low-carbon economy. The role of carbon-neutral methane in the energy mix is likely to play a significant role in the coming decades. The safe production, transportation and storage of methane are well managed as well the existing infrastructure has been in place for a long time without problems. We also have experience in the long-term operation of underground gas storage systems. Methane technology thus appears to be a very promising approach and, together with the functioning UGS infrastructure, could be an important step towards the potential use of biomethanation in underground gas storage facilities as a way to reduce greenhouse gas emissions in the future.

1. Introduction

In November 2018, the European Commission presented a long-term strategic vision to reduce greenhouse gas (GHG) emissions, showing how Europe can lead the way to climate neutrality - an economy with net-zero GHG emissions [1]. All feasible paths to a low-carbon economy and, eventually, net zero CO_2 emissions, require a massive increase in the role of electricity. The share of electricity in final energy demand will have to grow from around 20% today to around 60% by mid to late century. This electricity must derive from carbon neutral sources. While nuclear power and gas generation offset by carbon capture may play a role, three other sets of technologies will also be essential. First, hydrogen [2,3], ammonia [4,5], and methanol [4] will be used as energy carriers in transport and industrial applications and as chemical feedstock. These substances will eventually be produced synthetically, using electricity from renewables as the ultimate energy source. Second, biomass could provide low-carbon aviation fuel, or feedstock for plastic production [6,7]. The total scale of use, however, will need to be carefully managed to avoid harmful impacts on ecosystems and the food supply. Third, there should be at least some role for carbon capture, and either storage or use in key industrial processes such as cement production, where viable alternative routes to decarbonization are currently unavailable [8]. All these technologies are known as Power to X. Where Power means use of surplus electric power from renewable energy sources and the X means one of the above mentioned product (power-to-ammonia, power-to-chemicals, power-to-fuel, power-to-gas, power-to-hydrogen, power-to-liquid, power-to-methane, power to food, power-to-power and power-to-syngas). Power to Methane with biological methanization seems to be a promising technology which can be used worldwide [9]. Hydrogen from carbon-free energy combined with CO_2, e.g. from industrial exhaust gases, biomass or direct air capture, form a hydrocarbon with zero net greenhouse gas emissions. Power-to-Methane products can be stored and distributed through existing infrastructures (transmission/distribution) and used by existing

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facilities and applications. Therefore, it can contribute to one of the mayor issues in energy transition: the storage and transport of energy and may play a key role in future energy storage, together with other technologies [10]. Fig. 1 shows the storage capacity together with withdrawal periods of different energy storage systems. Today the only feasible option for long-term storage of large energy quantities is chemical energy storage. It becomes evident that the storage of Power to Methane product (biomethane) as well as hydrogen in the future in underground gas storage systems like aquifers, depleted hydrocarbon reservoirs and salt caverns will play an important role in future energy management.

To use the potential of underground gas storage (UGS) in the future for any type of energy storage or conversion, in our case by biological methanation, better knowledge of these systems is required. Deeper insights into the problematics of chemical processes and their biological catalysts in these environments have to be delivered for the possibility to implement new/alternative energy sources successfully. The topic of UGS, recently also UHS (underground hydrogen storage), was described in many scientific papers through different approaches. Published papers (Table A) present technological issues [12–14], site selection strategies [15–19], description of geological structures [20–22] and physical characteristics investigations [23–25] related to UGS. Some publications even describe topics related to microbial population dynamics modeling [26,27] or address the issues of microbial community composition in UGS [28–31] . Also, some very complex review articles including most of mentioned disciplines occur [32–35].

Nevertheless, the literature focused on an overview of microbiology in different deep subsurface environment related to UGS is still underrepresented. The objective of this review is connecting some technical and biological parts of this broad topic. Therefore, we aimed to describe different UGS environments inhabited by microbial communities involved in chemical processes, with a focus on methanogenesis. Furthermore, the bases of this field are mentioned as historical overview and evolution of UGS and an introduction to biogenic methane and its origin, and a description of the different types of UGS suitable for methanogenesis are given.

2. The biosphere in deep reservoirs

Due to its extremely hard accessibility, the scientific community did not pay much attention to the biosphere in deep reservoirs for a long time. However, in the meantime significant progress in microbiological studies has been made in the investigation of terrestrial habitats and therefore, a considerable rise in interest for the subsurface biosphere has emerged in the last four decades all over the world [28,36–39]. Most investigations were primarily induced by concerns about groundwater contamination or industrial activities like mining, nuclear waste repository search or interest in getting insights into the structure and processes in the deep reservoirs´ biosphere [40]. This interest led to a great uncovering of an abundant microbial life in deep reservoirs that can exist independent of solar-based energy sources [41]. Many types of natural or anthropogenically induced deep porous geological subsurface environments have been studied, both terrestrial [42–44] and the deep subsea floor [45]. In this review, we will focus on reservoirs related to UGS reservoirs and their role as biospheres for microbial communities.

3. Underground gas storage reservoirs

3.1. Historical overview

Employing deep reservoirs as a gas storage has a long and prosperous history. We may consider Canada as a pioneer country in this field, where the first successful UGS was built in 1915 in the partially depleted gas field in Welland County, Ontario [20,34]. About one year later, the second oldest natural gas storage (Zoar field) was built in New York (USA), which is still in operation today [46]. These countries were the first to perceive the economic potential and feasibility of underground storage and laid the technological foundations for this industry. The main factors in the development of gas storage activities were the growth of the gas market, the gradual discovery of new gas production fields associated with the need for transport to consumption sites and seasonal fluctuations in gas consumption [35]. An important increase in UGS number was registered in the post-World War II era, which was mainly induced by technological constrictions with piping capacity. Further progress in gas storing was recorded in Kentucky in 1946 where the aquifer was first employed as an UGS [20]. Solution-mined caverns in Michigan were first used as UGS in 1961 and the salt dome in Mississippi was first employed in 1970 as backup for hurricane disruption [47]. In 2018, there were 689 UGS facilities in operation worldwide (Fig. 2) [46].

Microbiological investigations of UGSs proved the presence of viable microorganisms [48] and their considerable influence in bio/geo-chemical processes in these environments [49]. Probably one of the first locations where changes of town gas composition during storage

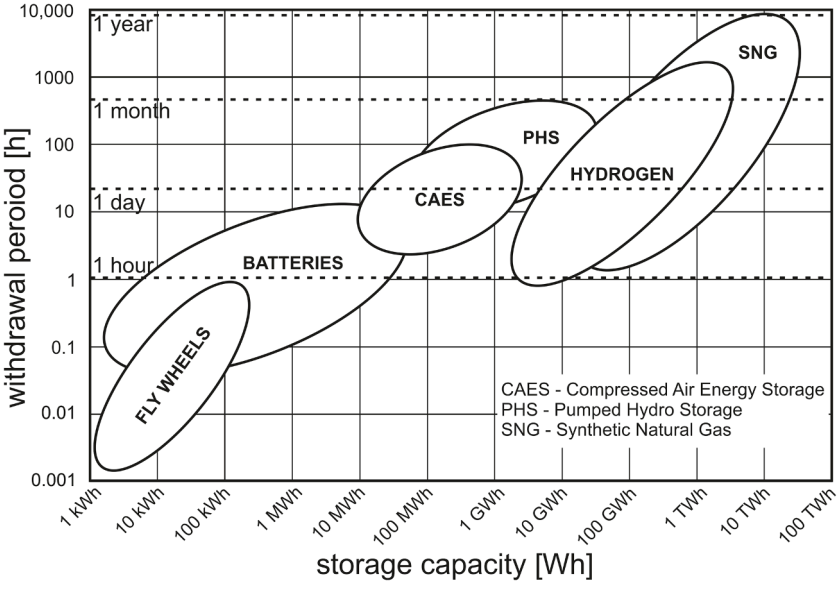

Fig. 1. Storage capacity of different energy storage systems [11] (modified by Vítěz).

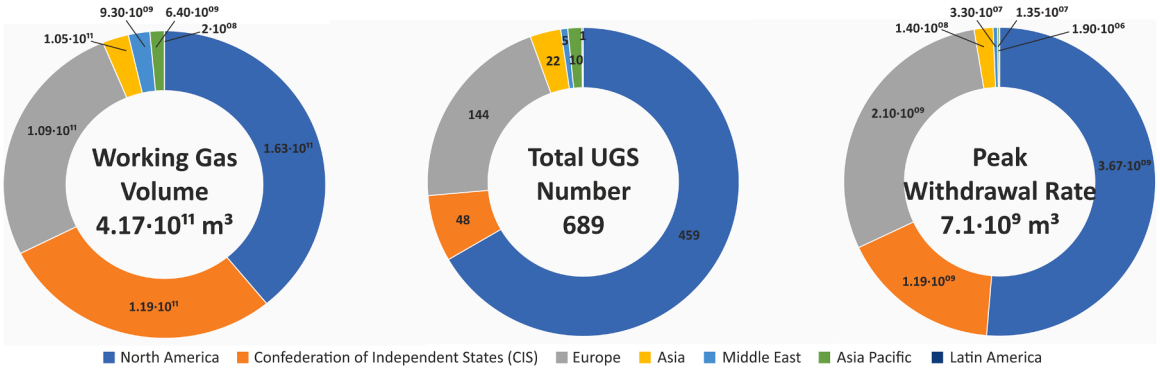

Fig. 2. Underground Gas Storage in different regions: total number, stored volume, peak withdrawal capacity [46].

were observed was in UGS Lobodice, Czechia. Part of the compositional changes were induced by microorganisms [39] responsible for a decrease in H_2 and CO_2, an increase in CH_4, and simultaneously a volume contraction. Šmigáň pointed out the possibility of microbial communities inhabiting the UGS storage layer. This observation was later supported by the cultivation of methane-producing microorganisms present in UGS water samples and by isotopic gas analyses [48], which was used for determining the gas origin [50].

Later, this phenomenon was also later observed in other UGSs and confirmed the fact that the process of microbial methanogenesis is common in quite similar environments [51,52]. With the emergence of molecular biology and the increase in research possibilities, knowledge gaps about uncultivated microorganisms could be filled. Today, the use of advanced molecular techniques like 16S-rRNA-profiling or metagenomic analysis enable the identification of microorganisms by genetic material from the UGS reservoir water. With this knowledge, the vision of the energetic potential of UGS (power-to-gas/methane technologies) was rebuilt, and new projects were started and the research interest in this field was boosted [53–56].

3.2. Microbial versus thermogenic gas reservoirs

In the Van Krevelen diagram (Fig. 3) there are visible four types of Kerogen in a process of organic matter maturation. In general, the Van Krevelen diagram shows the chemical evolution of immature kerogen of varying composition at increasing levels of thermal maturity [57]. While the original van Krevelen diagrams characterize source rock organic matter on a plot of atomic O/C versus atomic H/C from elemental analysis, the modified van Krevelen diagrams use the oxygen versus hydrogen index (OI versus HI) from Rock-Eval pyrolysis. Both diagrams can be used to assess the kerogen type. However, using the hydrogen index (being faster, cheaper, and requiring smaller sample amount) can underestimate kerogen quality, because highly oil-prone kerogens yield high atomic H/C, but do not always show correspondingly high pyrolytic yields [58].

Regarding the involvement of methanogens and the formation of biomethane, the first three types are important especially in the phase of diagenesis and maybe at the beginning of catagenesis. In the case of geological environments depending on geothermal gradient, it corresponds to relatively low temperatures up to 50–70 °C and a depth reaching up to 1.5 km.

The processes leading to reservoir traps fulfilment and the original gas containment of reservoirs play an important role before their conversion to UGS. The early burial stage of the organic matter is mainly influenced by microbial activities and characterized by low pressures and temperatures. The formation of biogenic methane has been recognized for a long time, but only within the last few years has it been realized that many gas reservoirs are of biogenic origin (Appendix). The difference between microbial and thermogenic reservoirs is too raw but indicates the opportunities for methanogens to populate the rock environment and consequently influence chemical and isotopic changes in stored gas. In many cases the reservoir containment is formed by mixtures of different gas origins or generation which may include biomethane and even the gases being generated in the late stage of maturation, metagenesis.

Other important factors to produce microbial methane during diagenesis are anoxic conditions, sufficient TOC and a sulfate depleted environment [60,61].

Microbial methane is typically produced in an immature stage of organic matter transformation. Under specific conditions, methanogens populating a porous rock environment can persist in reservoirs for extremely long periods and later create, based on injected gas composition, chemical changes according to their metabolic pathways.

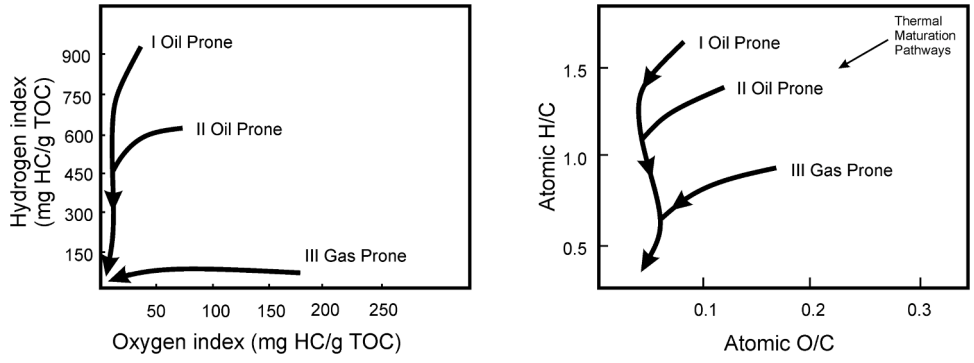

Fig. 3. Van Krevelen diagram, a) Classification of Kerogen Type (Oxygen and Hydrogen index); b) Classification of Kerogen Type by (H/C and O/C ratio) [59] (modified by Vítěz 2021).

3.3. Types of UGSs

Underground gas storage reservoirs play an important role in the energy market. The key UGS phenomena are seasonal, weekly, daily balancing between production and consumption, security of supply increase, optimization of hydrocarbon production and transport, gas price stabilization etc. Nowadays several types of UGSs are used [32,34,62]. Underground storage of natural gas requires specific geological conditions as geological structures and hydrocarbon traps which have to be sealed or separated enough from its surrounding to prevent gas leakage. In terms of storage mode, the UGS can be divided into three types of facilities [32]. These underground facilities are depleted oil and natural gas reservoirs, aquifers, and caverns being created in salt diapirs. The most common natural gas storages have been developed in depleted natural gas reservoirs (Fig. 4). Aquifers are usually preferred in areas where hydrocarbon fields or reservoirs are missing, similarly, leaching of caverns is based on local geological options and requirements for volume and withdrawal rates.

According to geologic and hydrodynamic features, the depleted oil and gas fields and aquifers are UGSs of the porous/fractured type, while the nonporous types, i.e. caverns, are usually leached in salt diapirs [20]. The highest number of UGSs can be found in North America. The total volume of UGSs in North America is about 163 bcm (billion cubic meters), which makes North America the area with the biggest UGS volume in the world. In Europe 143 UGSs have a total volume of about 109 bcm (Fig. 2) [46].

Other options are lined or unlined hard rock storage and abandoned mines, which are rather specific and rare solutions [34], but it could be soon on rise, because of higher demand for hydrogen storage in future. Preferentially in the regions where depleted reservoirs, aquifers, and salt deposits are not available this option can play an important role in the future [32]. These types of storage are not going to be discussed in this review in detail, same as the water curtain technique, lined hard rock and refrigerated mined caverns with respect to the lack of relevance to the methanogenesis process.

3.3.1. Storage in porous media

3.3.1.1. Depleted gas or oil reservoirs/ fields. Depleted gas or oil fields are the most common and frequently used type of UGS because of its economic feasibility and already available techniques and infrastructure. It is a withdrawn or partly withdrawn hydrocarbon accumulation located a few hundred up to approx. two thousand meters below the surface.

The operation is possible by one to maximum two cycles of injection and withdrawal per year [63].

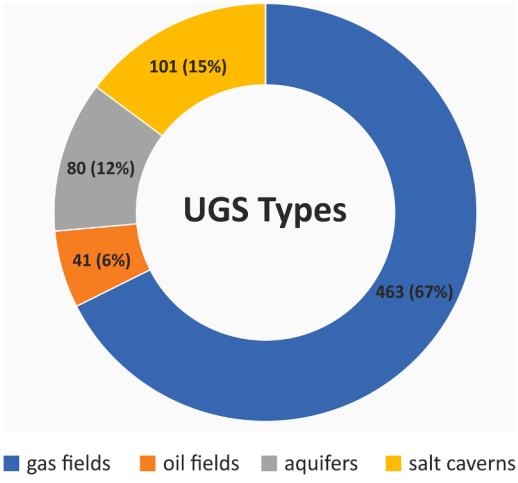

Fig. 4. The number of underground gas storages by type and percentual proportion [46].

General considered parameters for the establishment of new reservoirs are based on geological data analyses and physical parameters of geological structures. Considered factors are size and shape of the geological structure, size of aquifer layer, gas- water phase (in case of depleted or partly depleted storages), properties of reservoir and surrounding rock. Most important physical parameters are: i) porosity (the higher the better), ii) permeability which expresses the flow rate of liquid or gas (higher can enable better storing properties), and iii) water saturation which is best as low as possible (in case water saturation is high decreases the available volume for injection). Another important factor is drive mechanism which represents the move of whole gas volume in the reservoir rock. It depends on aquifer ability to move gas-water phase in reservoir rock caused by filling or emptying phase. In stable depletion drive reservoir is water-gas face relatively persistent in both injection and extraction periods. In such reservoirs the performance is high and minimal problems in production occur. The opposite case is a water driven reservoir where the performance is limited because of water production and its rising in production phase. In water driven reservoirs it is necessary to push water downward with high pressures [62].

Depleted fields dominate stored gas volume with a share of about 70% of total gas volume stored in UGSs. In total, 504 UGSs of this type were in use worldwide (Fig. 4) [46]. Employing the depleted or partially depleted oil reservoir has characteristics close to gas reservoirs except for the process of secondary oil recovery.

Under certain circumstances is possible to recover the own oil production which is added value to storage project itself. In this case it is necessary to remove the fraction of liquid hydrocarbons after the gas extraction before it is distributed into transport network [62]. The similar situation, but with remaining gas in a depleted gas reservoir, can be of advantage because it can serve as cushion gas. On the other hand, it can be deemed as a disadvantage if the remaining gas is able to reduce the purity of hydrogen [63]. Potential storing sites are already working e.g. in Argentina, Austria, UK, Poland, Germany [32].

3.3.1.2. Aquifers. Aquifers are an additional option to depleted reservoirs or complete alternative of storage. For aquifers, a basic requirement is a porous rock layer with a proper anticlinal or adequate shape and suitable petrophysical parameters, filled with water at a depth of hundreds to approx. two thousand meters [47]. The required geological properties of an aquifer are similar with depleted gas reservoirs with emphasis on porosity, permeability, formation pressure and sufficient capacity. To establish a UGS in an aquifer requires previous thorough geological investigation and higher investment. Emphasis is mainly placed on suitable tightness of caprock vertically and a shape of the structure with a spill point position preventing gas leakage. These criteria must be precisely determined and confirmed in advance. High price of realization is caused mainly by expensive geology survey, costs for infrastructure building and equipment as injection device, wells and pipelines [20] and price for cushion gas, which could be up to 80% of total gas volume injected in aquifer [64]. Gas injection and withdrawal is made once a year, sometimes twice, typically before or in winter season, when the gas demand is expectably the highest [63]. In 2018, there were 80 aquifer UGS facilities active worldwide (Fig. 4) [46]. Examples of worldwide potential storing sites are found in Germany, France, Czech Republic, Canada and Poland [32].

3.3.2. Storage in non-porous media

Salt caverns. Another option for natural gas storage is caverns leached in suitable salt formations. Salt formations occur in two forms, as domes characterized by greater depths than shallower located salt bedded deposits. New caverns are obtained through solution mining [65,66], dissolving the salt formations by injecting fresh water and extracting the

formed saline water [34]. The obtained cavern is enclosed by a salt layer, which forms an impermeable barrier and prevents gas leakage. It has special geological features as tightness and suitable mechanical properties with chemical resistivity of salt by this creating mechanical stability suitable for medium as well for short-term storage. In this type of UGS it is possible to make multiple (up to 10) cycles of injection and withdrawal of gas per year [63]. Salt caverns can be barely equal to previous options in terms of volume but are ideal to meet the demand for peak load cycling. Important factors as access to technical water and existing pipelines have to be considered in advance. In comparison with other types of underground storages, the cost to build such caverns are definitively lower [32].

UGS in salt caverns is on the rise and is currently responsible for about 9% of the total volume of stored underground gas. In total, 101 salt caverns were in use (Fig. 4) worldwide in 2018 [46]. The occurrence of this type is abundant in the US, in the region of the Great lakes where there is no other option of storing, and along the Gulf coast where there is plenty of salt domes [34]. Some are found in Canada and in Europe, comprising the following countries: UK, USA, Romania, Germany, Poland, Turkey and Denmark [32].

Recently salt caverns are also considered to be useful for hydrogen storage, because of the specific geological features mentioned above. However, their potential for methanogenesis is rather limited due to high salinity of brines and limited pore space to be populated [67]. Due to the difficult physicochemical conditions for methanogenesis causing its low efficiency, the topic will be not discussed in detail in this review. The salt caverns storage importance has been well described in different literature [63,66,68–70].

4. Environmental factors for biological methanogenesis

The deep porous reservoir environment in UGSs is influenced by several factors, most of which are determined by geological conditions. These usually strictly anaerobic habitats are suitable for methanogenic archaea that are capable of methanogenesis within a redox potential between −0.2 V and −0.4 V [71]. Other abiotic factors influencing the growth capacities are temperature, salinity, and pH. These variables have a direct impact on microorganisms' presence and composition in UGSs. The optimal temperature for methanogenesis, based on conditions and microbial community structure in the environment, is considered within the range of 27–47 °C for mesophilic and 50–80 °C for thermo- and hyperthermophilic methanogens (highly depending on the species). However, some methanogens can be active even at temperatures exceeding 100 °C [72] and can survive a pressure of more than 800 bar [73]. Nevertheless, a suitable pressure could be up to 150 bar [52,74]. Salt concentrations also impacts methane production. Most methanogens are limited to lower salinity, typical for hydrogenotrophic and acetoclastic species. Certain observations showed positive correlation between increasing salinity (within the range 3.5–8 mM Cl^- and 1.75–47 mM Na^+) and methane production rates. Nevertheless, an extremely high salinity level may inhibit many methanogens or support highly adapted halophilic species [75]. Considering the optimal pH, most species are adapted to environments with pH close to a neutral value [76]. Nevertheless, alkaliphilic [77] or acidophilic species are also documented [78,79].

Despite an effort to describe ideal biochemical conditions for methanogens in general, the natural variability and different adaptations among this functional group provide a wide spectrum of possible habitats with various environmental demands.

5. Microbial processes in deep subsurface environments

In the deep subsurface, the lack of light as an energy source points to a photosynthesis-independent system [80]. Microbial life here depends either on energy sources available in the surrounding rock or in dissolved components transported by water fluctuation. The geological bodies used for UGS are deep subsurface formations where microbial processes follow the specific spatial pattern linked to the gradual decrease of oxygen levels that lead to an anaerobic environment. In aquifers, this sequence of terminal electron-accepting processes may occur at a depth of meters or even kilometers. Usually, molecular hydrogen serves as an electron donor for these microbial communities. With gradual oxygen depletion, five ways of microbial metabolisms can be found: nitrate and manganese reduction, ferric iron reduction, sulfate reduction and finally methanogenesis [81,82].

5.1. Denitrification

The process of denitrification, as a part of the nitrogen cycle, is carried out mainly under anoxic conditions [83]. It is the reduction of nitrate and nitrite as terminal electron acceptors to nitrous oxides and finally nitrogen gas. A broad range of inorganic substrates (thiosulfate, H_2, CH_4) may serve as electron donors. Each step of this metabolic pathway is catalyzed by complex multisite metalloenzymes [84]. The enzymes include nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductase [85]. Among the denitrifiers, the main representatives are Bacteria, but halophilic and hyperthermophilic archaea as well as some fungi are able to perform denitrification as well [86].

5.2. Iron and manganese reduction

The metabolic pathway of iron reduction is considered one of the evolutionary oldest forms of microbial respiration [81]. In the facultative anoxic environment, the microorganisms capable of utilizing Fe (III), as a terminal electron acceptor, are usually present. This group of DIRB (dissimilatory iron reducing bacteria) are Fe (III) reducers and they are often capable of Mn (IV) reduction, too [87,88]. In this process, Fe (III) is reduced to Fe (II), and Mn (IV) to Mn (II). A wide variety of organic compounds (acetate, aromatic compounds, and long chain fatty acids) serve as electron donors [89,90], which are then often completely oxidized to carbon dioxide. Among this phylogenetically diverse group, representatives of the domains Bacteria and Archaea are included. One important role in subsurface environments is given to the *Geobacteraceae* family, namely *Geobacter metallireducens* [87], which is involved in bioremediation processes and is the most investigated one [88]. Other typical representatives include *Shewanella* and *Pseudomonas* species or relatives [37] like *Pseudomonas stutzeri* which was isolated from a copper mine environment. This bacterium is capable of dissimilatory Fe (III) and nitrate reduction under facultative anoxic conditions [91].

5.3. Sulfate reduction

Sulfate reducers are strictly anaerobic microorganisms and are therefore only found in zones with low redox potentials [92,93]. They utilize a variety of organic compounds or H_2 as electron donors. The final product of this metabolic pathway is the H_2S gas. In subsurface environments, this process is mainly limited to the availability of organic carbon. Here, the discharge of organic pollutants like hydrocarbons or sulfide may play a role [94]. The sulfate reduction is catalyzed by the enzyme ATP sulfurylase and the first product of the pathway is adenosine 5-phosphosulfate (APS), followed by the reduction of APS to sulfite or bisulfite [95,96]. Subsequently, sulfite is reduced via sulfite reductase that results finally in H2S generation [97]. Sulfate reducers are represented by a diverse group of microorganisms mostly consisting of Bacteria and members of the hyperthermophilic archaeal genus *Archaeoglobus*. Typical representatives of SRB can be found in the genera *Desulfotomaculum, Desulfovibrio, Desulfobacter, Desulfococcus*, etc. (all desulfo- prefix named genera). Some thermophilic genera also occur among the Bacteria including *Thermodesulfobacterium* and *Thermodesulfovibrio* [98,99].

5.4. Methanogenesis

In zones of extremely low oxidation–reduction potential, where all other favorable electron acceptors such as oxygen, nitrate, sulfate and iron are depleted or absent, methanogenesis occurs [100]. This last step in the degradation of organic matter is executed by Archaea, which play a key role in the global carbon cycle accounting to more than half of all methane produced on Earth per year [101]. Methanogenesis is also considered a dominant metabolic pathway in very deep aquifers [92].

The key enzyme performing the final step in the process, the reduction of a methyl group to methane, is the methyl coenzyme M reductase A (mcrA). Three different types of methanogenesis are described: the hydrogenotrophic, the methylotrophic, and the acetoclastic pathway (Fig. 5). Nevertheless, some of the methanogenic archaea can use multiple pathways [102]. The typical substrates are fermentation products such as H_2 and CO_2, acetate and methylated compounds formed by their syntrophic partners as by-products of organic matter breakdown [74,103]. Methanogens ensure the maintenance of energetically favorable conditions for syntrophy by the oxidation of acetate and hydrogen [104].

5.4.1. Hydrogenotrophic metabolic pathway

The hydrogenotrophic pathway, where CO_2 is reduced with H_2 as an electron donor, is the most common one. Typical representatives of hydrogenotrophic methanogens are species from orders *Methanobacteriales, Methanomicrobiales*, or *Methanococcales*. At first, the reduction of CO_2 and activation to formyl-methanofuran takes place, while ferrodoxin in its reduced form serves as the electron donor [106]. In the second step, the formyl group is transferred to tetrahydromethanopterin (H4MTP). Afterwards the dehydrated and reduced formyl group, the methylene-H4MTP, is formed with a subsequent reaction to methyl-H4MTP reduced by F420 (F420H2) as an electron donor. Then the methyl group is transferred to coenzyme M (CoM) followed by reduction to methane with coenzyme B (CoB) as an electron donor takes place. The result of this reaction is a heterodisulfide (CoM-S-S-CoB), which is reduced with H_2 for reuse of the coenzymes [100,107]. There are several methanogens capable of using formate instead of H_2 as an electron source for the reduction of CO_2. Then the difference occurs in the first step of the pathway, where formate dehydrogenase oxidizes four formate molecules to CO_2. The reduction of one CO_2 molecule to methane follows [107]. Similarly, a few methanogens can also use alcohols (ethanol, 2-propanol) as electron donors [108,109]. Other species as *Methanosarcina barkeri* and *Methanothermobacter thermautotrophicus* can use CO for methanogenesis, where CO dehydrogenase (CODH) oxidizes four molecules of CO to CO_2. Then the one molecule of CO_2 is reduced to methane with H_2 as an electron donor [110]. Therefore, both methanogens are still capable of growth on H_2 and CO_2. The exception is *Methanosarcina acetivorans* which also grows on CO. This species is missing the function of a hydrogenase system thus it is unable to grow on H_2 and CO_2.

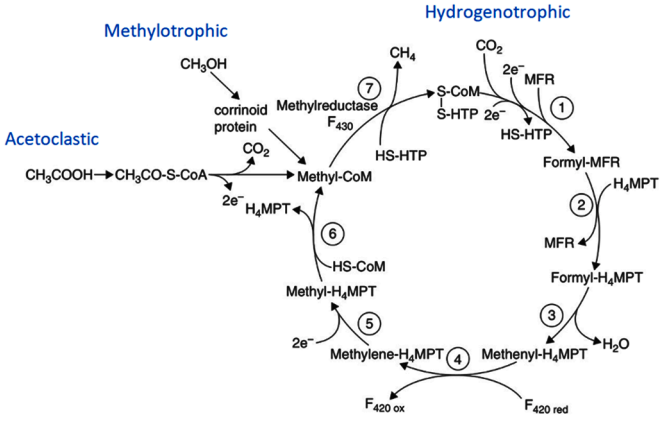

Fig. 5. The pathway of methane formation from acetate, methanol, and CO_2. MFR – methanofuran; CoB – coenzyme B; H4MPT – tetrahydromethanopterin; HS-CoM – coenzyme M. 1 – activation of CO_2, binding to MFR; 2 – transfer of formyl group to H4MPT; 3 – conversion of formyl group to methenyl; 4 and 5 – reduction of carbon to methyl group; 6 – transfer of methyl group to coenzyme M; 7 – reduction of methyl to methane [105].

5.4.2. Acetoclastic metabolic pathway

This pathway utilizes disproportionation, where acetate is divided, while the methyl group is fixed. The carbon in the methyl group is reduced to methane, while the carbon atom in the carboxyl group is oxidized to CO_2. This pathway is typical for members of the order *Methanosarcinales* like *Methanosarcina* sp. and *Methanothrix* sp. The first step of the acetoclastic pathway is characterized by the activation of acetate into acetyl-coenzyme A (acetyl-CoA), from which a methyl group is then transferred into the central methanogenic pathway.

The *Methanosaetaceae* family uses the acetyl-CoA synthetase pathway, while members of the *Methanosarcina* genus use a different pathway (acetate kinase and phosphoacetyl transferase) for the synthesis of acetyl-CoA. Consequently, carbon monoxide dehydrogenase uses acetyl-CoA and catalyzes the split into CoA and a methyl group, which is transferred (via tetrahydromethanopterin or tetrahydrosarcinapterin) to CoM and finally reduced to CH_4 by methyl-CoM reductase [111].

5.4.3. Methylotrophic metabolic pathway

Finally, the methylotrophic pathway comprises the different types of methanogenesis by using various substrates as methanol, methylamines or methylated compounds like methanethiol and dimethyl sulfide. It is mainly represented by members of the orders *Methanosarcinales* and *Methanomassiliicoccales*. The process starts by the transfer of the methyl-group from the methylated substrate to a corrinoid protein by a substrate-specific methyltransferase (MT1). Afterwards the C1 group is transferred to HS-CoM by another methyltransferase (MT2), and methyl-CoM is formed [112]. One methyl-CoM is oxidized to CO_2 (via the hydrogenotrophic pathway in reverse) generating the reducing equivalents to reduce three methyl-CoM to methane and generating a proton motive force [113]. Within the acetoclastic pathway, the disproportionation reaction occurs. This leads to the reduction of three molecules of methanol to CH_4 and the oxidation of one molecule of methanol to CO_2, but only in cases where hydrogen is not consumed. A typical example for this pathway is *Methanosphaera stadtmanae* growing only on methanol and H_2 [114]. Other species utilize methanol only in the presence of H_2. These includes *Methanomassiliicoccus* sp. or *Methanosarcina barkeri* [115,116]. Still others use only methanol, incapable of growing autotrophically on H_2/CO_2 (e.g. *Methanosarcina horonobensis*) [117].

5.5. Syntrophy in methanogenesis

Global cycling of carbon in anaerobic environments is based on a complex community of metabolically coupled microorganisms that are highly adapted to the environment. Anaerobic syntrophy is defined as a thermodynamically interdependent extreme lifestyle where the degradation of an organic compound occurs only if end products (usually hydrogen, formate, and acetate) are maintained at very low concentrations. In contrast to syntrophy under aerobic conditions, only little is known about the key steps in anaerobic syntrophic food chains.

Syntrophy is crucial for the complete conversion of a wide range of natural polymers such as polysaccharides, proteins, nucleic acids, and lipids to CO_2 and CH_4. The first step of conversion is provided by fermentative bacteria, which hydrolyze the polymeric substrates and metabolize the hydrolysis products to acetate and longer fatty acids, CO_2, formate, and H_2. Propionate, fatty acids, alcohols, some amino acids and aromatic compounds are consequently syntrophically

metabolized to the methanogenic substrates H_2, formate, and acetate [118]. The hydrogenotrophic and the acetoclastic methanogens complete the process by converting acetate, formate, and hydrogen produced by other microorganisms to methane and carbon dioxide. Microbial syntrophy between Bacteria and methanogenic archaea improves the methanogenic activity and methane yield [119].

Only two processes for methanogenesis from acetate are described. The first one is acetoclastic methanogenesis. The second process is based on syntrophic mutualistic reactions and there is a lack of information about this syntrophic metabolism involved in oxidation of acetate to hydrogen and carbon dioxide catalyzed by syntrophic acetate oxidizing bacteria (SAOB). Possible SAOB can facilitate acetate consumption and could be coupled with hydrogenotrophic methanogenesis (SAO—HM) [120]

In the first step via syntrophic acetate oxidation (SAO), the methyl and carboxyl group of acetate are oxidized to CO_2 and H_2 as end products. Many SAO bacteria belong to *Clostridia*, e.g. *Clostridium ultunense, Thermoacetogenium phaeum* or *Syntrophaceticus schinkii* [121]. This reaction is energetically extremely unfavorable and requires a close partnership with methanogens or other hydrogenotrophs. The complete syntrophic reaction is exergonic and the total Gibbs free energy change is the same as for acetoclastic methanogenesis [122].

A special habitat for syntrophic growth of methane-producing Archaea can be found in the subsurface in context with natural oil degradation. With respect to the lack of electron acceptors as oxygen and nitrate, syntrophic methanogenesis and sulfate reduction are the dominant processes in oil biodegradation [123]. Hydrocarbon degradation coupled to sulfate reduction is the dominating process over methanogenesis if sulfate is present at concentrations higher than 50 μM [124]. Many sulfate reducing microorganisms can switch their metabolism to fermentative oil degradation, producing short chain fatty acids, hydrogen and carbon dioxide means they can grow with sulfate as an electron acceptor or as fermenters in association with methanogens when sulfate is depleted like members of the genera *Desulfovibrio, Desulfotomaculum,* and *Archaeoglobus*. Methanogenic oil degradation is an exclusively syntrophic process and syntrophic interactions are not confined to a specific phylogenetic group of prokaryotes [125–127]

6. Exploring the microbial communities in different UGS environments

6.1. Aquifers

Aquifers are natural geological underground bodies characterized by porous structures saturated with water. Nowadays they are mainly used as water or gas storage facilities. The principal factors influencing underground microbial life are the chemical composition of aquifer water, pressure and temperature. The salinity influences the presence of halophiles, while the sulfate content affects sulfate-reducing bacteria [43, 128,129]. Higher levels of iron ions support the growth of iron-reducing microorganisms [92,130].

One of the first microbiological research targeting methanogens was realized in the Magothy aquifer in Bay Park, New York (127 to 146 m depth). Different types of microorganisms, including methanogens, where found in an abundance of 102–103 cells/100 ml. Based on their morphology, the detected microorganisms were determined as organisms belonging to the genus *Methanobacterium*. SRBs were not present in any aquifer from water samples [131]. Deeper boreholes (411 to 415 m) were investigated in Florida, where the decrease in nitrate was recorded at the expense of the abundance of other forms of nitrogen [132]. In different aquifers in North Carolina, which were in an environment contaminated by wastewater from dimethyl-phthalate production (contained aromatic compounds, 1.5% acetate, 0.5% formate and 0.05% methanol), the emerging gas contained 60% of methane. The surveyed methanogens belonged to the genera *Methanobacterium* and *Methanococcus* [133], but strong evidence as the presence of substrates for acetoclastic and methylotrophic pathways in wastewater and taxonomical changes in past decades are now pointing to the genus *Methanosarcina*. The detection of methane in another borehole without the influence of pollutants hints to a natural occurrence of methanogenic archaea in these aquifers. Biogenic methane was also detected in an aquifer town gas reservoir in Lobodice, Czechia. After reservoir injection, changes in town gas composition appeared over time. The amounts of hydrogen, carbon dioxide and carbon monoxide decreased while the amounts of methane increased [39]. The subsequent microbiological analysis confirmed the abundance of mesophilic methanogenic archaea in this environment. Isolate description referred to hydrogenotrophic rods forming aggregates, probably belonging to the genus *Methanobacterium* [48]. Another series of experiments conducted in Sweden, Äspö Hard Rock Laboratory (68 to 446 m depth) revealed that methane was produced, determined from underground water samples, in constant abundance throughout one year of sampling [134]. The microorganisms' morphology corresponded to the *Methanosarcina* genus for shallow depths, while the whole depth profile was characterized by members of the genus *Methanobacterium*, later specified as *Methanobacterium subterraneum* [135].

Recent findings applying sequencing methods open up the opportunity of a closer look into microbial community composition *in situ*. In the Mahomet aquifer Illinois, a phylogenetical trend across sampled boreholes occurred. With increasing amounts of sulfate, decreased values of dissolved methane were measured [128]. It is typical when favorable conditions for SRB prevail, that they can easily overgrow methanogens. Interestingly, sequencing of 16S rRNAs obtained from this habitat also showed numerous representatives of the *Thaumarchaeota* phylum. Furthermore, sequences of methanogens (order *Methanosarcinales*), *Thermoplasmata*, and even some sequences related to ANME-2D were detected in lower numbers. In addition, also *Crenarchaeota* sequences could be obtained [128].

The presence of *Thaumarchaeota* and the predominant occurrence of members of the *Methanobacteriales* was also confirmed by groundwater sampling in Japan [136] and Pennsylvania [137]. Numerous wells with a maximum depth of 130 m were sampled. Gene sequencing for archaeal 16S rRNA and mcrA were used. The genes for the mcrA enzyme are highly conserved, hence its usage in molecular biology for methanogens determination is typical. The sequencing results detected the presence of members of the families *Methanomicrobiaceae* and *Methanoregulaceae* (order *Methanomicrobiales*) and a high abundance of representatives of *Methanomassiliicoccales*. Similar results were obtained by sampling a high temperature aquifer in Japan. Based on the isotopic composition of methane, the thermogenic and microbial origin of methane was confirmed and the inoculation of water samples from the well led to a continuous formation of methane in the gas phase. Samples from a depth of 1 km were analyzed for the 16S rRNA gene and resulted in sequences of methanogens from the order *Methanobacteriales*. The sequences obtained had an approximate similarity of 95% to the species *Methanobacterium aarhusense* and *Methanobacterium alcaliphilum*. These species are able to grow in the temperature range present in the aquifer, namely 40.3–44.4 °C. In addition, some sequences showed a similarity of 99.4% to *Methanothermobacter thermoautotrophicus* [138].

The Underground Sun Storage project, recently in progress in Austria, is targeting the task of attempting to apply Power to Gas (PtG). The investigation conducted on formation water of the test field comprising this project showed shifts in consortia due to hydrogen exposure in reactors. The dominance of members of the *Firmicutes* phyla was detected across the three-year sampling. Later they were overgrown by methanogens comprised up to 60% of active microbial community in the fourth year of the experiment. In addition, the syntrophic relationship of methanogens and phylum *Atribacteria* was assumed.

6.2. Oil fields

Oil fields are associated with the occurrence of natural gas. Typically,

the accumulated oil at the interface is extracted first, while the natural gas is exploited afterwards. Large numbers of microorganisms break down complex hydrocarbons, particularly in aerobic processes [139]. The anaerobic degradation in oil deposits is linked to iron, nitrate or sulfate reduction [140–144] whereas the reduction of carbon dioxide to methane forms the final step in the biodegradation process [145–147]. Due to the presence of sulfate-reducing organisms, strong suppression of methanogenesis occurs in the presence of sulfate and sulfur-rich oil compounds [142]. The anaerobic degradation itself is characterized by slow kinetics and many unknown process pathways [148,149]. The markers considered in this process are mainly 2-naphthoic acid and its alkylated forms or alkylated succinates [142,150–152]. The main zone, where the degradation takes place, is located at the water-oil interface [145,153]. Here the principal pathway recorded is hydrogenotrophic methanogenesis together with syntrophic processes [146,149,154], where functional consortia of Bacteria and Archaea are formed. In this mutual cooperation, the exchange of substances supports decomposition on one hand and the production of methane on the other. Among the syntrophic organisms, members of the bacterial phylum *Synergistetes* are found, which generate acetate, CO_2, and hydrogen [141,142,148,149, 155,156]. Other detected phyla were *Firmicutes, Proteobacteria* and *Thermotogales* which inhabit numerous representatives of hydrogen producers [138,157].

The temperature of the oil field reflects the community of microorganisms present there. Oil fields with temperatures of 80 °C and higher preclude growth of many bacterial species with degrading ability, and many thermophilic bacteria as well. On the contrary, mesophilic representatives occur in oil fields with an average temperature of around 30 °C [146,149]. The bacterial genera *Thermoanaerobacterium, Anaerobaculum* and *Thermoacetogenium* have repeatedly been captured in samples while mixed cultures have been obtained from boreholes which are known to have syntrophic relationships with methanogenic archaea [157,158].

Temperature manifests itself as an important factor in archaeal community composition. The representatives of hydrogenotrophic thermophiles from oil fields are members of the genus *Methanothermobacter* dominating high-temperature reservoirs [142,148]. In addition representatives of the genus *Methanothermococcus* have been isolated from a Louisiana oil field in the USA [140]. As a methylotrophic representative, *Methermicoccus shengliensis (Methanosarcinales)* was found in an oil well in China [159]. Among the mesophilic representatives isolated from this environment are the genera *Methanosarcina., Methanomassiliicoccus* and *Methanomethylovorans* as well as various members of the order *Methanomicrobiales* [141,148,160,161]. In particular in a Louisiana oil field, *Methanohalophilus* halophilus and representatives of the order *Methanobacteriales* could be identified [140]. Furthermore, two new species have been isolated in Japan, from the sediment of an oil tank: *Methanobacterium petrolearium* and from the pipeline leading to brine saturated with natural gas *Methanobacterium ferruginis* [162].

6.3. Salt caverns

Salt caverns are artificially created reservoirs with diverse types of stored substances, which could be typically methane, oil sand extraction waste [67] or recently considered and tested CO_2 and H_2 [70,163].

The determining factor of the environment is the salinity of the brine in the cavern, which sometimes even reaches saturation level of NaCl [164]. Very few microorganisms are capable of growth under these extremely high salt conditions. Bacterial strains collected from salt caverns often include sulfate-reducing bacteria of the genera *Desulfovibrio, Desulfovermiculus* and *Desulfotomaculum*, which tolerate sodium chloride concentrations of up to 21.5% [67]. *Halobacteria* are archaeal microbes that grow aerobically and are dependent on solar energy. Under anaerobic conditions, only fermentative growth on arginine has been reported under these circumstances [165]. Anaerobic archaea that are able to grow in salt caverns are methanogenic representatives from the family *Methanosarcinaceae* [166–168]. Salt tolerant species include members of the genera *Methanohalophilus, Methanolobus, Methanomethylovorans* and *Methanosalsum* [166–169]. A recent study on salt tolerance genes from a hypersaline solar saltern even porposes a novel genus within the *Methanosarcinaceae*, the halophilic *Methanosalis* [170].

Detailed research conducted on two types of caverns provided a closer look into microbial community composition. A cavern for waste from oil sands extraction revealed a predominance (up to 70% of gene copies) of *Methanomicrobia* class members. The dominant genera there were again *Methanohalophilus* and *Methanolobus*, followed by members of the phyla of *Firmicutes* (mostly represented by *Halanaerobium*), and *Proteobacteria*. In contrary, an unused cavern showed significantly different results influenced by a hundred times higher sulfate concentration (2020 ppm) compared to caverns in use. Up to half of the gene copy number belonged to the class *Clostridia*, followed by the class *Deltaproteobacteria* and an archaeal community predominantly consisting of the class *Methanomicrobia*. Other representatives from the *Methanococci, Thermococci*, and *Halobacteria* classes were also present. The genera with the highest abundance were represented by *Acetohalobium (Clostridia)*, then *Desulfovermiculus* and finally the methanogenic *Methanohalobium*. However, these genera occurred in a small fraction in another unused cavern, too [67].

These results indicate the possible changes in microbial composition due to cavern utilization and provide a look at original microbial communities of salt-rock formations and water present there. However, outward contamination by injected gas has to be considered.

7. Conclusion

The global climate change is and will be one of the major challenges for the next decades. It is well documented that the increase of the CO_2 concentration in the atmosphere has an anthropogenic origin. As a major factor power plants that use fossil fuels (coal, oil or even natural gas) are being deactivated incrementally. However, due to an increasing worldwide population in combination with a rising demand of energy (mainly electricity) powerful alternatives are urgently necessary. Renewable energies like wind or solar energy are not continuously available. Therefore, storage facilities for these alternatives are absolutely important. It seems, that the Power-to-Gas technology could be such a technique, by producing molecular hydrogen by water electrolysis and converting it with CO_2 from different sources to methane. This methane can be stored and distributed through existing infrastructures (transmission/distribution) and used by existing facilities and applications. Methanogenic archaea are the key players in this PtG process. Meanwhile, these microorganisms are known since more than 40 years and a great variety of strains has been studied. They exhibit broad spectra of adaptations to environmental conditions, like temperature, pH, or salt concentrations. This is an important advantage, since it will not be possible to apply the Power-to-Gas technique in a global scale in fermenters or conventional reactors. Here, *in situ* conversion of H_2 and CO_2 in underground facilities can play the key-role in the near future. The great advantage of an PtG application in UGS facilities is not only scaling, but also the transformation of a common repository into a storage and production unit. The different types of these, in most cases former natural gas deposits, have been outlined in this review with their specific geological, chemical and physical characteristics, exhibiting their advantages and disadvantages.

Surprisingly, all of these aquifers, salt caverns as well as oil fields and coal mines are housing an immense diversity of microorganisms. Studies of this often called “deep biosphere” are still quite rare, but an increasing interest in such habitats, also for biotechnological applications, makes it necessary to investigate these biotopes. Especially molecular investigations demonstrate that even complex mutual communities are present in the storage facilities. Methane-producing archaea, necessary for the Power-to-Gas technology, could be found in the majority of such

habitats and were represented by an impressive variety of phylogenetic types. This is in line with former publications, that in UGS facilities a decrease of H_2 and CO_2, combined with a decrease in pressure occurs, but simultaneously an increase of methane was obtained. This demonstrates that methanogenic archaea are not only present in such habitats but are also metabolically active.

However, metagenomic data sets need to be critically judged to avoid misinterpretation of contaminated gases. The gas stream is carried through long pipes and can be contaminated with microorganisms from biogas plants or other reservoirs that are in turn introduced into the surveyed cavern. The presence of specific microbial DNAs alone is therefore no proof for a living organism or a metabolic activity in the cavern. Therefore, sampling of the reservoirs and cultivating of living organisms from the deep subsurface, however, is absolutely necessary, although very challenging due to technical restrictions (high pressure, depth of the caverns). Advanced sampling techniques are needed to cultivate and confirm the presence of microbes responsible and suitable for underground biomethanation.

The sources of carbon-neutral CO_2 and H_2 are still limited and expensive. Carbon dioxide can be obtained from biogas plants, food and beverage industry or direct air capture, which makes this gas a very limited and localized resource. In contrast, hydrogen gas is needed in four-times larger amounts than CO_2 and can be produced by electrolysis. This process requires a large amount of energy from renewable sources and is therefore still expensive, but with the extension of the capacities of renewable energies, this may be possible in the near future. The pricing for biomethane from the subsurface not only depends on the expenses for educt gases, but also on the individual locality, carbon taxes and political conditions. For example, the amount of hydrogen that can be introduced into established gas infrastructure is limited and varies between countries and states. This condition may improve with hydrogen economy and the focus on bioeconomic solutions. Meanwhile, we suggest to aim for a gradual substitution of fossil gas with biomethane to a scale that is manageable with the actual given regulations.

The interesting question is in fact to what extent is it necessary to influence and control of the microbial process in the UGS facilities. Here, corresponding studies are completely missing, but due to the fact that such conversion processes have already been observed without external influence, it is likely that after detailed analyses of different characteristics of an UGS, Power to Methane processes can be carried out with high efficiencies in such locations.

With these findings, we suggest that underground storage facilities like aquifers and depleted reservoirs can be suitable as massive, invisible bioreactors for the production of biomethane using PtG. A careful review of physical, chemical and geological data is meaningful to evaluate the suitability of the UGS for biomethanation. With that a simple solution for a green alternative to fossil natural gas could be integrated into existing gas infrastructures.

Salt caverns are known to inhabit several microbes, but to date no methanogens with a salt tolerance of a saturated sodium chloride solution are known. Initially, these systems seem to fit for future hydrogen storage due to the absence of halotolerant methanogens. However, stored hydrogen could still face a change in gas composition caused by other microorganisms naturally present in the subsurface. These changes could not only lower the gas quality, but also induce microbial corrosion due to the production of toxic hydrogen sulfide and other disruptive metabolites. This fact must be considered and evaluated in detail for prospective hydrogen storage projects.

Ultimately, three questions remain: i) is it possible to inject high amounts of molecular hydrogen produced by water electrolysis from renewable energies in combination with the necessary amounts of CO_2 (that means 25% of the amount of H_2) in the UGS systems, ii) to what extend is it possible and necessary to control the process in the UGS systems by influencing the activities of the different microorganisms, especially those of the methanogenic archaea naturally present in these habitats and iii) is there long-term influences in the storage like the sealing of porous material due to large cell mass.

Therefore, still intensive interdisciplinary research activities are needed, to make this highly promising storage technique working in the future, the sooner the better, because time for saving our climate is running short!

CRediT authorship contribution statement

Anna Molíková: Conceptualization, Formal analysis, Writing – original draft. **Monika Vítězová:** Conceptualization, Writing – review & editing, Supervision, Project administration. **Tomáš Vítěz:** Conceptualization, Formal analysis, Writing – original draft, Visualization. **Iva Buriánková:** Conceptualization, Formal analysis, Writing – original draft. **Harald Huber:** Conceptualization, Writing – review & editing, Supervision. **Linda Dengler:** . **Nikola Hanišáková:** Investigation, Writing – original draft, Visualization. **Vladimír Onderka:** Investigation, Writing – original draft, Supervision. **Iva Urbanová:** Investigation, Writing – original draft.

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Declaration of Competing Interest

None.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.est.2021.103631.

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